Rheology and ultrasonic properties of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ liquid

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The equilibrium and nonequilibrium viscosity and isoconfigurational shear modulus of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ supercooled liquid are evaluated using continuous–strain-rate compression experiments and ultrasonic measurements. By means of a thermodynamically-consistent cooperative shear model, variations in viscosity with both temperature and strain rate are uniquely correlated to the variations in isoconfigurational shear modulus, which leads to an accurate prediction of the liquid fragility and to a good description of the liquid strain-rate sensitivity. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2732822]

The Pt–Ni–Cu–P bulk-glass forming system[1] is known to form one of the toughest bulk metallic glasses to date,[2–4] characterized by a fracture toughness value of ~ 80 MPa m$^{1/2}$. The inherent toughness of this system is shown to be a consequence of its tendency to undergo extensive shear-band networking prior to fracture.[2] This tendency has been primarily attributed to its high Poisson's ratio (~ 0.42), which designates that the material favors accommodation of stress by shear. Interestingly, Poisson's ratios of metallic glasses were recently shown to be directly correlated to the rheology of their undercooled liquid state, and specifically to the liquid fragility.[5] In a recent rheological study[6] it is demonstrated that Pt-based liquid is indeed one of the most fragile metallic glass-forming liquids, which to some extent explains its inherently tough nature. In the present study we employ continuous–strain-rate compression experiments and acoustic measurements in conjunction with a recently developed cooperative shear model[7–9] to assess the rheology and ultrasonic properties of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ liquid under equilibrium and nonequilibrium conditions.

The rheology of the supercooled liquid was assessed using the continuous–strain-rate compression setup described in a previous study.[10] The alloy ingot was prepared by first prealloying Pt (99.9 mass %), Ni (99.9 mass %), and Cu (99.99 mass %) by induction melting, and then alloying P (99.999 mass %) by stepwise furnace heating. The specimens were prepared by first fluxing the alloy with B_2O_3, and subsequently casting it into 4 mm diameter rods, whose amorphous nature was verified by thermal analysis. The rods were cut and polished to produce 4 mm tall cylindrical specimens. The typical 2:1 geometric ratio was not adopted here, as the 1:1 ratio was found more appropriate for geometrically constraining the specimens against unusually excessive barreling (possibly related to a high Poisson's ratio). The compression experiments were performed for an adequate duration to ensure that a steady-state flow stress had been attained. The strain-rate dependent viscosity measured in the temperature range of 473 to 523 K is presented in Fig. 1. The strain-rate dependence exhibits the typical trend observed in other glass forming systems: in the low strain rate limit, viscosity is stabilized at the Newtonian limit characterized by a strain-rate sensitivity exponent of 1.0; in the high strain rate limit, viscosity is stabilized at a non-Newtonian limit characterized by a strain-rate sensitivity exponent of ~ 0.1.

The isoconfigurational shear modulus at the high-frequency "solidlike" limit is evaluated using ultrasonic measurements along with the density measurements.[11] Shear wave speeds were measured using the pulse-echo overlap setup described previously.[8] Densities were measured by the Archimedes method, as given in the American Society for Testing and Materials Standard C693-93. Measurements were performed *ex situ* on the amorphous specimens at room temperature, after being quenched rapidly from the processing temperature. The isoconfigurational shear moduli at the processing temperatures were then estimated by extrapolating the room temperature measurements using a linear Debye-Grüneisen constant to account for the thermal expansion effect on the shear modulus of the frozen glass. A measured linear Debye-Grüneisen coefficient of ~ 13 MPa/K for $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ was utilized.[12] We measured the temperature-dependent equilibrium isoconfigurational shear modulus by performing ultrasonic measurements on relaxed undeformed specimens annealed at temperatures between 472 and 503 K. We also measured the strain-rate dependent nonequilibrium isoconfigurational

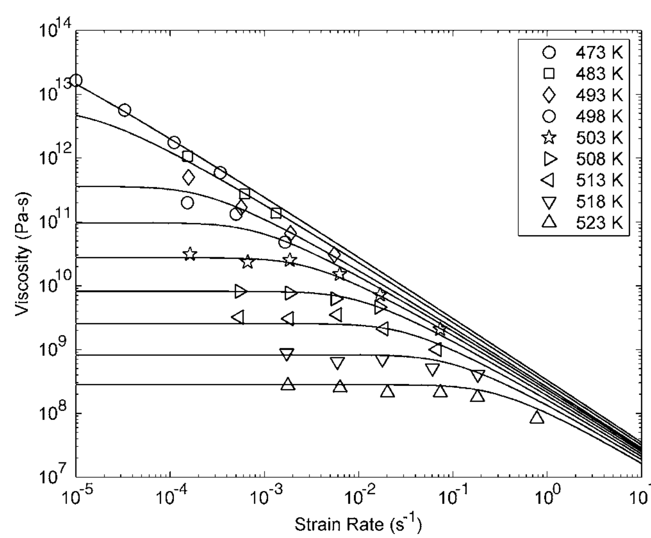

FIG. 1. Viscosity of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ at the indicated temperatures and strain rates assessed from continuous-strain-rate compression experiments. Lines are fit to the data using the kinetic balance formulation given in Eq. (4).

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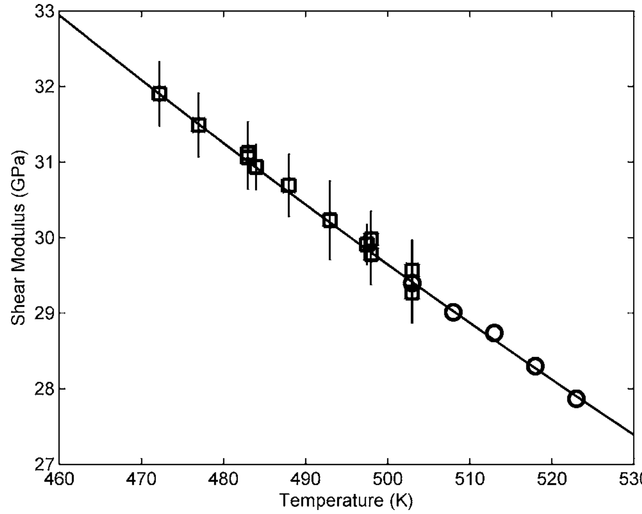

FIG. 2. Acoustically measured shear modulus (corrected for the Debye-Grüneisen effect) of the relaxed equilibrium liquid annealed at the indicated temperatures (□). Predicted equilibrium shear modulus from measured equilibrium viscosity data using Eq. (1) (○). The line is a fit to the data using the temperature dependence relationship given in Eq. (2).

shear modulus by performing ultrasonic measurements on specimens deformed at 473 K and strain rates between 1×10^{-5} and 3.4×10^{-4} s^{-1}. The thermal annealing process as well as the deformation process was performed for several Maxwellian relaxation times to ensure that a steady configurational state had been attained, while the succeeding quenching process was performed as rapidly as possible in order to freeze that configurational state. The results for the ultrasonically measured shear modulus corrected for the Debye-Grüneisen effect are presented in Fig. 2 for the equilibrium liquid annealed at the indicated temperatures, and in Fig. 3 for the nonequilibrium liquid deformed at the indicated rates.

In several recent studies,[7–9] a thermodynamic link between the isoconfigurational shear modulus G and viscosity η has been proposed as follows:

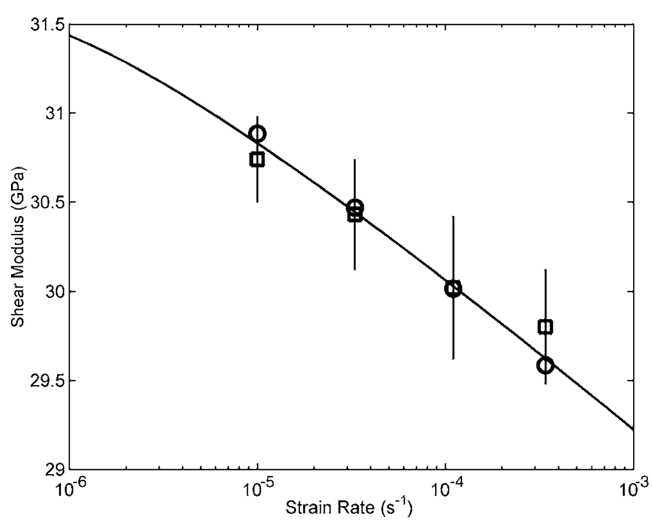

FIG. 3. Acoustically measured shear modulus (corrected for the Debye-Grüneisen effect) of the nonequilibrium liquid deformed at 473 K at the indicated strain rates (□). Predicted nonequilibrium shear modulus from measured nonequilibrium viscosity data using Eq. (1) (○). The line is a fit to the data using the kinetic balance formulation given in Eq. (4).

$$\frac{G}{G_g}=\left[\frac{T}{T_g}\frac{\ln(\eta/\eta_\infty)}{\ln(\eta_g/\eta_\infty)}\right]^q, \tag{1}$$

where T_g is the glass transition temperature, $\eta_g\equiv10^{12}$ Pa s is the equilibrium viscosity at T_g, G_g is the equilibrium shear modulus at T_g, and η_∞ is the Born limit of viscosity. The exponent q is defined in previous studies as $q=n/(n+p)$,[8,9] where n and p are the reduced "elastic" and "cooperative volume" fragility indices, respectively, which quantify the contributions of isoconfigurational shear modulus and cooperative shear volume to the softening of the shear flow barrier. In a similar analysis for the Zr-based bulk-glass forming liquid[8] it was determined that the best correlation between G and η is obtained when $n\cong p$, i.e., $q\cong1/2$. In the present analysis we take $q=1/2$ to hold for the $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ liquid as well. For this liquid we also take $T_g=489$ K (interpolated value at which $\eta_g\equiv10^{12}$ Pa s), $G_g=30.5$ GPa (interpolated value at T_g), and $\eta_\infty\equiv4.55\times10^{-5}$ Pa s (taken as the Planck's limit of viscosity). We can therefore use Eq. (1) to correlate the liquid viscosity evaluated from the mechanical tests to the liquid shear modulus measured acoustically. In Fig. 2 we superimpose the equilibrium shear moduli predicted from Newtonian viscosity data, while in Fig. 3 we superimpose the nonequilibrium shear moduli predicted from non-Newtonian viscosity data. As evidenced from these plots, the liquid viscosity can be very well correlated to shear modulus via Eq. (1).

A proposed thermodynamic relation for the temperature dependence of the equilibrium isoconfigurational shear modulus $G_e(T)$ can be utilized to fit the experimental data of Fig. 2 and determine the reduced elastic fragility index n for this liquid. This relation is given by[9]

$$G_e(T)=G_g\exp[n(1-T/T_g)]. \tag{2}$$

A fit to the equilibrium data of Fig. 2 yields $n=1.29$. Such a high value for the reduced elastic fragility places $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ among the most fragile liquids investigated using this treatment.[8,9] Specifically, the Angell fragility m can be estimated by relating m to n using $m=(1+n/q)\log(\eta_g/\eta_\infty)$;[8] which gives $m=59$, a value consistent with the fragilities reported previously for similar Pt-based liquids.[6]

In the context of this analysis, Non-Newtonian flow has been treated as steady nonequilibrium flow governed by a balance between the rate of dissipated mechanical energy density and the rate of barrier crossing events.[9] The barrier energy density W can be related to η and G as follows:

$$W=kT\ln(\eta/\eta_\infty)=W_g\left(\frac{G}{G_g}\right)^{1/q}, \tag{3}$$

where $W_g=kT_g\ln(\eta_g/\eta_\infty)$ is the equilibrium barrier energy density at T_g. The kinetic balance equation governing non-Newtonian flow is[8]

$$-\alpha\frac{(n/q)W_g}{T_g\Delta c_p}\eta\dot{\gamma}^2=\frac{(W-W_e)(W/W_g)^q}{\eta/G_g}, \tag{4}$$

where $\dot{\gamma}$ is the strain rate, Δc_p is the specific heat capacity change at T_g, $W_e(T)=W_g\exp[(n/q)(1-T/T_g)]$ is the equilibrium barrier energy density, and α is a model parameter. This parameter arises from treating the irreversible barrier crossing events as unimolecular Maxwellian relaxation processes, and in essence quantifies the deviation from that assumption.

For $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$, the measured $\Delta c_p = 2.56\ \mathrm{MJ/m^3}$ can be employed.[13] As shown in Figs. 1 and 3, Eq. (4) is capable of capturing nonequilibrium viscosity and shear modulus data reasonably well over the entire range of strain rates considered, for a parameter value of $\alpha = 37$.

In conclusion, by means of continuous-strain-rate compression experiments and ultrasonic measurements we evaluated the equilibrium and nonequilibrium viscosity and isoconfigurational shear modulus of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ supercooled liquid. By utilizing a thermodynamically-consistent cooperative shear model we correlated the variations in viscosity with both temperature and strain rate to the variations in isoconfigurational shear modulus, which led to an accurate prediction of the liquid fragility and to a good description of the liquid strain-rate sensitivity.

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